

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-041093

(43)Date of publication of application : 10.02.1997

(51)Int.Cl.

C22C 38/00

C22C 38/44

(21)Application number : 07-191983

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(22)Date of filing : 27.07.1995

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(54) HIGH STRENGTH MARTENSITIC STAINLESS STEEL EXCELLENT IN SULFIDE STRESS CORROSION CRACKING RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a high strength martensitic stainless steel excellent in sulfide stress corrosion cracking resistance in a severe corrosive environment as well as in hot workability by reducing C content in a 13%Cr steel and also regulating respective contents of contained elements.

SOLUTION: This steel has a composition which contains, by mass, 0.01-0.05% C, <0.30% Si, 0.30-1.20% Mn, <0.025% P, <0.003% S, 12.0-14.0% Cr, 3.0-5.5% Ni, 1.0-2.5% Mo, 1.0-2.5% Cu, 0.01-0.05% Al, 0.03-0.08% Ni, and <0.005% O or further contains 0.001-0.005% Ca and in which 13%Cr steel is used as a base and respective contents of C, S, Si, Al, and O are reduced and also proper amounts of Ni, Mo, Cu, N, and Ca are incorporated. By this method, the high strength martensitic stainless steel, excellent in hot workability as well as in sulfide stress corrosion cracking resistance even in a corrosive atmosphere containing CO₂, Cl ions, H₂S, etc., can be produced.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention about the high intensity martensitic stainless steel excellent in the sulfide-proof stress-corrosion-cracking nature used, for example as a steel pipe of the oil well of a crude oil, or the gas well of natural gas, It is related with the high intensity martensitic stainless steel excellent in sulfide-proof stress-corrosion-cracking nature suitable for using it as a steel pipe of the oil well with very severe corrosive environment which contains carbon dioxide (CO₂), a chloride ion (Cl⁻), hydrogen sulfide (H₂S), etc. especially, or a gas well.

[0002]

[Description of the Prior Art] It continues till recent years and the development to a depths oil field upon which it did not look back, the sour gas rice field where the corrosiveness by which 1 ** was abandoned has strong development, etc. prospers on a worldwide scale conventionally facing drain-izing of the petroleum resources predicted at a jump and the near future of an oil price. Generally such an oil field and a gas field have very deep depth, and the atmosphere serves as severe corrosive environment containing CO₂, Cl⁻, H₂S, etc. Therefore, as construction material of the oil well steel pipe used for mining of such an oil field or a gas field, the construction material which moreover has corrosion resistance and stress-corrosion-cracking-proof nature with high intensity is required.

[0003] Generally, under the environment containing CO₂ and Cl⁻, Cr martensitic stainless steel tube is used 13% which was excellent in CO-proof₂ corrosion resistance, CO-proof₂ stress-corrosion-cracking nature, and pitting-proof nature. However, the actual condition is that expensive 2 phase stainless steel is used in the environment where H₂S lives together further besides CO₂ or Cl⁻, from the sulfide-proof stress-corrosion-cracking nature of 13%Cr martensitic stainless steel being low. For this reason, in addition to CO-proof₂ corrosiveness, CO-proof₂ stress-corrosion-cracking nature, and pitting-proof nature, development of the 13%Cr martensitic stainless steel for oil well tubes which also has sulfide-proof stress-corrosion-cracking nature is desired strongly.

[0004]

[Problem(s) to be Solved by the Invention] CO-proof₂ corrosiveness which was excellent in this invention in view of the above-mentioned situation under the severe corrosive environment containing CO₂, Cl⁻, H₂S, etc., It aims at providing the high intensity martensitic stainless steel excellent in the sulfide-proof stress-corrosion-cracking nature

which has sulfide-proof stress-corrosion-cracking nature in addition to CO-proof ₂ stress-corrosion-cracking nature and pitting-proof nature.

[0005]

[Means for Solving the Problem] This invention persons CO-proof ₂ corrosiveness, CO-proof ₂ stress-corrosion-cracking nature, In order to fully improve the sulfide-proof stress-corrosion-cracking nature of the martensitic stainless steel paying attention to 13%Cr martensitic stainless steel considered to be suitable for an oil well steel pipe in respect of pitting-proof nature, Various kinds of experiments which investigate sulfide-proof stress-corrosion-cracking nature under environment which contains CO₂, Cl⁻, and H₂S about various alloy contents were conducted by having used Cr steel as a base 13%, and examination was repeated. As a result, good hot-working nature is secured by adding nickel, Mo, Cu, N, and Ca, and reducing S, Si, aluminum, and O further in the 13% Cr steel which reduced C more remarkably than before, and. It finds out that sulfide-proof stress-corrosion-cracking nature under above-mentioned environment is improved remarkably, and came to make this invention.

[0006]High intensity martensitic stainless steel excellent in the sulfide-proof stress-corrosion-cracking nature of this invention specifically, C: Less than more than 0.01mass%0.05mass% and less than Si:0.30mass%. Mn: Less than more than 0.30mass%1.20mass% and less than P:0.025mass%. S: Less than 0.003mass% and less than more than Cr:12.0mass%14.0mass%. nickel: Less than more than 3.0mass%5.5mass% and less than more than Mo:1.0mass%2.5mass%. Cu: Less than more than 1.0mass%2.5mass% and less than more than aluminum:0.01mass%0.05mass%. N: Contain less than more than 0.03mass%0.08mass% and less than O:0.005mass%, and the remainder consists of Fe and inevitable impurities.

[0007]Here, it is still more preferred to contain less than more than Ca:0.001mass%0.005mass%. Hereafter, it explains still in detail about martensitic stainless steel of this invention. First, a reason for steel composition limitation in this invention is explained.

[0008]Although C is an important element related to intensity of a martensitic stainless steel tube, sensitization in which corrosion resistance and mechanical properties deteriorate at the time of tempering happens easily by addition of the below-mentioned nickel. Since a manufacturing cost rose remarkably when C needed to be made less than 0.05mass% and C was made into less than [0.01mass%], in order not to make the sensitization start, C was made into 0.01 - 0.05mass%. In this invention, we decided to compensate strength reduction by reduction of C by addition of nickel so that it might mention later.

[0009]Although Si was an element required as a deoxidizer in the usual steel-manufacture process, since generating of a delta ferrite is caused, CO-proof ₂ corrosiveness is reduced and hot-working nature was also further reduced when 0.30mass% was exceeded, it made Si less than 0.30mass%. in order that Mn may secure intensity as a martensitic stainless steel tube for oil well tubes -- more than 0.30mass% -- although it was required, since it had an adverse effect on toughness when 1.20mass% was exceeded, Mn was made into 0.30 - 1.20mass%.

[0010]Although both P is elements which degrade CO-proof ₂ corrosiveness, CO-proof ₂ stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature and few [as much as possible] things of the content are desirable,

extreme reduction causes a rise of a manufacturing cost. It was industrial comparatively cheaply feasible, and P was made less than 0.025mass% as a range which does not degrade CO-proof₂ corrosiveness, CO-proof₂ stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature.

[0011] Although S was an element which degrades the hot-working nature of steel remarkably in a pipe manufacturing process and few [as much as possible] things were desirable, since pipe manufacture of it at the usual process was attained when reducing it to less than 0.003mass%, it made a maximum of S 0.003mass%. Cr(s) are the main elements for maintaining CO-proof₂ corrosiveness and CO-proof₂ stress-corrosion-cracking nature -- more than 12.0mass% from a corrosion-resistant viewpoint, although it is required, Since generating of a delta ferrite was caused and hot-working nature deteriorated when 14.0mass% was exceeded, Cr was made into 12.0 - 14.0mass%.

[0012] While nickel strengthens a protective film and improving CO-proof₂ corrosiveness, CO-proof₂ stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature, are added in order to raise intensity of 13% Cr steel which reduced C, but. Less than [3.0mass%], the effect was not accepted, but since it spoiled the stability of martensitic structure when 5.5mass% was exceeded, it made nickel 3.0 - 5.5mass%.

[0013] Although Mo is an element which gives resistance over pitting by Cl⁻ to steel, Less than [1.0mass%], since generating of a delta ferrite was caused and CO-proof₂ corrosiveness, CO-proof₂ stress-corrosion-cracking nature, and hot-working nature fell when it did not accept but 2.5mass% was exceeded, the effect made Mo 1.0 - 2.5mass%. Although it is an element which Cu strengthens a protective film, controls invasion of hydrogen to inside of steel, and improves sulfide-proof stress-corrosion-cracking nature, Less than [1.0mass%], since CuS carried out the grain boundary deposit at an elevated temperature and hot-working nature fell when the effect was not acquired but 2.5mass% was exceeded, Cu was made into 1.0 - 2.5mass%.

[0014] Although aluminum had powerful deacidification, less than [0.01mass%] was not enough as an effect of the deacidification, and since it had an adverse effect on toughness when 0.05mass% was exceeded, it made aluminum 0.01 - 0.05mass%. Although N was an element which raises pitting-proof nature remarkably, less than [0.03mass%] was not enough as an effect of pitting-proof nature, and since various nitrides are formed and toughness was degraded when 0.08mass% was exceeded, it made N 0.03 - 0.08mass%.

[0015] O is a very important element in order to fully demonstrate performance of steel of this invention. That is, if there is much the content, in order to form various kinds of oxides and to reduce remarkably hot-working nature, CO-proof₂ corrosiveness, CO-proof₂ stress-corrosion-cracking nature, pitting-proof nature, sulfide-proof stress-corrosion-cracking nature, and toughness, O was made less than 0.005mass%. By fixing S as CaS and spheroidizing inclusion S system, Ca makes small a lattice strain of a matrix in the circumference of inclusion S system, and has the operation which lowers trap ability of hydrogen. Less than [0.001mass%], the effect was not remarkable, and since an increase in CaO was caused and CO-proof₂ corrosiveness and pitting-proof nature fell when 0.005mass% was exceeded, it made Ca 0.001 - 0.005mass%.

[0016] Although steel of this invention has the above component composition, a place which reduced S, Si, aluminum, and O remarkably from a viewpoint of hot-working nature especially in addition to corrosion resistance and stress-corrosion-cracking-proof

nature has the big feature. Therefore, in manufacturing an oil well steel pipe using steel of this invention, it can manufacture, without modifying the usual manufacturing process in any way. That is, after fabricating steel of this invention to a seamless pipe or an electroseamed steel pipe, in order to heat to temperature within the limits of 950-1050 ** with rolling, to cool with water cooling or air cooling and to obtain intensity required as an oil well steel pipe after that, usually it anneals at temperature within the limits of 550-650 **.

[0017]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described. The ingredient and experimental result of steel of this invention are shown even in Table 4 with them of a comparative example from Table 1. Although A steel (the steel expressed with the sample sign A is said, and it is the same as that of the following) is the 13%Cr martensitic stainless steel corresponding to an API (U.S. Japan Petroleum Institute) standard among comparison steel and B steel to L steel adjusts a chemical entity based on A steel, One of ingredients separates from the range of this invention steel. M steel to V steel is this invention steel which adjusted the chemical entity based on A steel.

[0018]After fully carrying out degasifying of the molten steel of these chemical entities, it was considered as a 100-K steel ingot, and the with the outer diameter of 83.8 mm (3.3inches) and a thickness of 12.7 mm (0.5inches) pipe was produced using the model seamless rolling mill for research. Subsequently, air cooling was carried out, after cutting down each piece raw material of a pipe blank test and heating at 1000 ** for 1 hour. As shown even in Table 4 from Table 1, it annealed at three kinds of temperature about each steel, respectively, and yield strength was adjusted to the level of 690 - 965MPa (100 - 140ksi) except for A steel. Each yield strength is shown even in Table 4 from Table 1. From the specimen raw material annealed in this way, 3 mm in thickness, 30 mm in width, a corrosion spool 40 mm in length, 2 mm in thickness, 20 mm in width, the piece of U-bending testing of stress corrosion cracking 75 mm in length, and the constant stress tensile stress corrosion-cracking specimen whose diameter of a parallel part is 6.4 mm were produced by machining, respectively. The examination was presented with the piece of U-bending testing of stress corrosion cracking, changing into the state where bending stress was given to the direction of board thickness ($t= 2$ mm), as [set / bend the specimen 1 and / to 8 mm / with the jig 2 / the **** radius R], as shown in drawing 1. Each examination was carried out on the following conditions.

[0019](1) Corrosion test NaCl:20% solution, CO₂:30 atmosphere, Temperature: 200 **, period:two-week U-bending [(2)] testing-of-stress-corrosion-cracking NaCl:20% solution, CO₂ partial pressure:30 atmosphere, temperature:200 **, period:two-week constant-stress [(3)] tensile stress corrosion-cracking examination (sulfide testing of stress corrosion cracking)

NACE solution (5%NaCl+0.5%CH₃COOH+H₂O), H₂S partial pressure : 0.01 and 0.1 atmosphere (CO₂ was mixed and it balanced), pH: 2.8 and 3.5 (addition of CH₃COONa adjusted), load-stress:100% yield strength, temperature: In 24 ** and a period:one-month corrosion test, the existence of pitting generating was investigated by the corrosion rate calculated from the decrease of weight of the specimen, and 10 time magnifying glass observation. In U-bending testing of stress corrosion cracking, the existence of the crack generation was investigated by macro-scopic observation and the observation by optical microscope of the section. The existence of the fracture within predetermined time was

investigated in the constant stress tensile stress corrosion-cracking examination. The result of these each examination is collectively shown even in Table 4 from Table 1. [0020]As shown even in Table 4 from Table 1, the ghost-proof stress-corrosion-cracking nature of A steel corresponding to an API standard is inferior, and comparison steel from B steel to L steel may be excellent in respect of CO-proof ₂ corrosiveness, CO-proof ₂ stress-corrosion-cracking nature, and pitting-proof nature compared with A steel, but. Sulfide-proof stress-corrosion-cracking nature does not improve. On the other hand, this invention steel from M steel to V steel excels comparison steel in CO-proof ₂ corrosiveness, CO-proof ₂ stress-corrosion-cracking nature, and pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature is improved especially. The degree of this improvement is still larger in Ca addition steel from R steel to V steel, although Ca additive-free steel from M steel to Q steel is also large enough. Namely, adaptation by the environment of lower pH and a higher H₂S partial pressure is possible for this invention steel which added Ca also in the environment containing the same H₂S. Whether Ca addition steel is adopted or Ca additive-free steel is adopted should determine by pH of an oil well or a gas well, and the conditions of the H₂S partial pressure. Thus, this invention steel is understood that it is usable enough as an oil well steel pipe in the oil well environment containing H₂S. At the time of pipe manufacture, surface discontinuity occurred and C steel especially whose Si, S, and O are outside the range of this invention, respectively, E steel, and K steel were inferior to the pipe inner surface side in hot-working nature.

[0021]
[Table 1]

区分 記号	化 学 成 分 (mass%)										焼成度 (°C ×1h)	強度 (MPa)	腐食度 (ε ^{η²} ·h)	腐食試験 孔食	*硫化物応力腐食割れ試験			
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	N	O	Ca	**0.01	0.1	0.01	0.1	
A	0.210	0.55	0.61	0.018	0.0020	13.1	—	—	0.022	0.021	0.0070	—	700	612	3.340	●●●●●●●●●●	—	
B	0.053	0.25	0.59	0.021	0.0022	13.1	4.2	1.0	1.5	0.025	0.051	0.0033	0.0032	650	653	3.240	●●●●●●●●●●	—
C	0.025	0.33	0.81	0.016	0.0018	13.0	4.0	1.1	1.3	0.024	0.055	0.0041	0.0028	600	638	3.310	●●●●●●●●●●	—
D	0.031	0.22	0.80	0.024	0.0025	13.2	3.9	1.0	2.0	0.030	0.046	0.0038	0.0015	575	1011	0.035	○○○○○○○○○○	—
E	0.021	0.26	0.62	0.020	0.0035	13.1	4.1	1.0	1.5	0.031	0.052	0.0039	0.0022	625	625	0.112	●●●●●●●●●●	—
F	0.041	0.20	0.62	0.021	0.0023	11.7	4.2	1.5	2.0	0.035	0.045	0.0041	0.0026	600	575	0.071	○●●●●●●●●●●	—
比 較														600	680	0.068	○●●●●●●●●●●	—
例														625	801	0.080	○○○○○○○○○○	—
														600	907	0.134	●●●●●●●●●●	—
														625	829	0.161	●●●●●●●●●●	—
														575	976	0.112	●●●●●●●●●●	—
														600	907	0.112	●●●●●●●●●●	—
														625	829	0.161	●●●●●●●●●●	—
														575	952	0.071	○●●●●●●●●●●	—
														600	880	0.080	○○○○○○○○○○	—
														625	801	0.080	○○○○○○○○○○	—
														575	987	0.154	●●●●●●●●●●	—
														600	920	0.132	●●●●●●●●●●	—
														625	836	0.136	●●●●●●●●●●	—

**：●発生有り、○：発生無し、*：H₂ S分圧（気圧）

[0022]
[Table 2]

区 分 号	化 学 成 分 (mass %)										焼 成 温 度 ($^{\circ}\text{C}$ $\times 10$)	降伏強 度 (MPa)	腐食速 度 (kg/m^2 $\cdot \text{h}$)	腐食試 験 孔食 度	* 硫化物腐食割れ試験		
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	N	O	Ca	* pH = 3.5 CO ₂ 应力腐 食割れ	* pH = 2.8 CO ₂ 应力腐 食割れ		
G 0.025	0.25	1.01	0.018	0.0018	13.5	2.5	1.5	1.5	0.023	0.059	0.0038	0.0035	575	863	○	● ●	
H 0.021	0.20	0.60	0.018	0.018	0.027	13.1	4.1	0.8	1.3	0.024	0.038	0.0028	0.0035	600	801	● ○	● ○
I 0.026	0.26	0.58	0.015	0.0025	13.2	4.8	2.2	0.5	0.023	0.048	0.0042	0.0028	625	764	○	● ○	
J 0.025	0.25	0.60	0.012	0.0023	13.2	5.3	2.0	2.0	0.063	0.051	0.0048	0.0018	575	949	● ○	● ○	
K 0.026	0.28	0.77	0.021	0.0020	13.1	4.5	2.0	1.5	0.024	0.027	0.0041	0.0015	600	918	○	● ○	
L 0.031	0.24	0.80	0.017	0.0025	13.5	4.5	2.1	1.5	0.030	0.048	0.0053	0.0021	625	859	● ○	● ○	

*: ●発生有り、○: 発生無し、**: H₂ S 分圧 (気圧)

[0023]
[Table 3]

区 記 分 号	化 学 成 分 (mass%)										燃 燒 溫 度 (°C ×1h)	強 度 (MPa)	腐 食 速 度 (g/m ² ·h)	腐 食 力 度 孔 食 試 驗 U 曲 折 試 驗 CO ₂ 腐 食 試 驗 PH = 3.5	腐 食 力 度 孔 食 試 驗 PH = 2.8	* 硫化物应力腐食割れ試験									
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al															
M	0.021	0.15	1.10	0.015	0.0026	13.0	3.5	2.3	1.5	0.015	0.023	0.0022	-	575	947	0.029	○	○	-	○	○	○	○	●	●
N	0.025	0.25	0.47	0.021	0.0021	12.5	3.2	1.2	2.2	0.025	0.044	0.0046	-	600	883	0.030	○	○	-	○	○	○	○	●	●
本 銹 G	0.031	0.27	0.66	0.018	0.0025	13.5	4.0	1.1	1.3	0.035	0.046	0.0041	-	625	843	0.028	○	○	-	○	○	○	○	●	●
明 P	0.035	0.28	0.80	0.020	0.0013	13.2	4.7	2.0	1.0	0.021	0.052	0.0035	-	575	932	0.040	○	○	-	○	○	○	○	●	●
明 例	0.042	0.02	0.71	0.024	0.0008	13.8	4.3	1.5	1.9	0.043	0.056	0.0028	-	600	952	0.036	○	○	-	○	○	○	○	●	●
Q	0.042	0.02	0.71	0.024	0.0008	13.8	4.3	1.5	1.9	0.043	0.056	0.0028	-	625	890	0.032	○	○	-	○	○	○	○	●	●

* : ●発生有り、○: 発生無し、** : H₂S分圧(気圧)

[0024]

[Table 4]

区 分 記 号	化 学 成 分 (mass %)										焼 き 度 ($^{\circ}\text{C}$ \times h)	降 伏 強 度 (MPa)	腐 食 試 験 度 (g/m^2 \cdot h)	腐 食 速 度 (g/m^2)	*炭化物应力腐食割れ試験					
	C	Si	Mn	P	S	Cr	Ni	Mo	Ca	N					* $\text{H} = 0.01$	0.1	0.01	0.1		
R 0.021	0.15	1.11	0.015	0.0025	13.0	3.5	2.2	1.4	0.015	0.033	0.0023	0.0012	575	936	0.030	○	○	○	○	
S 0.026	0.26	0.47	0.020	0.0021	12.4	3.1	1.2	2.2	0.025	0.045	0.0046	0.0021	625	814	0.026	○	○	○	○	
T 0.031	0.26	0.66	0.018	0.0026	14.5	4.1	1.0	1.3	0.034	0.046	0.0041	0.0032	575	939	0.029	○	○	○	○	
U 0.035	0.27	0.81	0.021	0.0012	13.2	4.6	2.0	1.1	0.021	0.005	0.0034	0.0043	600	903	0.030	○	○	○	○	
V 0.043	0.02	0.71	0.024	0.0009	13.9	4.4	1.5	2.0	0.043	0.065	0.0028	0.0048	625	814	0.029	○	○	○	○	
発 明 例														575	937	0.030	○	○	○	○

*: ●発生有り、○: 発生無し、**: H₂ S分圧(気圧)

[0025]

[Effect of the Invention] The high intensity martensitic stainless steel which was excellent in the sulfide-proof stress-corrosion-cracking nature of this invention as explained above, C content to the Cr steel reduced more remarkably than before 13% nickel, Mo, Cu, And N is added, by reducing S, Si, aluminum, and O further shows good hot-working nature, sufficient corrosion resistance and stress-corrosion-cracking-proof nature are shown under the severe corrosive environment which contains CO_2 , H_2S , and Cl^- further, and, moreover, high intensity can be secured. Therefore, it can be conveniently used as steel for oil well steel pipes used under the above harsh environments.

[Translation done.]